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<p>(54) Title: INTEGRAL ION-EXCHANGE COMPOSITE MEMBRANES</p>		
<p>(57) Abstract</p> <p>An integral composite membrane is provided including a porous polymeric membrane impregnated with a perfluoro ion-exchange material to make the micropores of the membrane occlusive. A method for making the integral composite membrane is also provided.</p>		

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TITLE OF THE INVENTION

INTEGRAL ION-EXCHANGE COMPOSITE MEMBRANES

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a regular application of Provisional Application No. 60/015,514, filed April 30, 1996.

10

FIELD OF THE INVENTION

An integral composite ion-exchange membrane is provided which is useful in electrolytic processes and other chemical and physical separations.

15

BACKGROUND OF THE INVENTION

Ion-exchange composite membranes (IEM) are used in fuel cells as solid electrolytes. A membrane is located between the cathode and anode and transports protons formed near the catalyst at the hydrogen electrode to the oxygen electrode thereby allowing a current to be drawn from the cell. These polymer electrolyte fuel cells are particularly advantageous because they operate at lower temperatures than other fuel cells. Also, these polymer electrolyte fuel cells do not contain any corrosive acids which are found in phosphoric acid fuel cells.

25

Ion-exchange composite membranes are also used in chloralkali applications to separate brine mixtures to form chlorine gas and alkali hydroxide. The membrane selectively transports the alkali metal ions across the membrane while rejecting the chloride ions.

30

Additionally, IEMs are useful in the areas of diffusion dialysis, electrodialysis and for pervaporation and vapor permeation separations.

35

In electrodialysis, electrolytes can be divided into a concentrated and a diluted stream. This can be accomplished by arraying anionic and cationic exchange membranes in a filter press arrangement. Alternating compartments between the membranes are filled with either the feed stream or the product stream. An electric field is applied across this series array by inserting electrodes in the end compartments.

In diffusion dialysis, a stream of contaminated acid or base can be separated from dissolved metal ions, colloidal or non-ionic species. The acid

or base can then be returned to the original process. A diffusion dialysis system may consist of a filter press type arrangement with anion or cation exchange membranes between compartments of that system. Alternate compartments are filled with either the waste material or water. The desired
5 ions diffuse through the membrane. The undesired ions are rejected and removed as waste.

IEMs must have sufficient strength to be useful in their various applications. For example, IEMs that are not reinforced (such as those commercially available from E. I. DuPont de Nemours, Inc., and sold under the
10 registered trademark Nafion®) are inherently weak. Often the need for increased strength requires the membranes to be made thicker which decreases their ionic conductance.

As seen below, fluorinated ion-exchange polymers having carboxylic acid and/or sulfonic acid functional groups, and salts thereof, are known, as is their
15 use in fuel cells and chloralkali electrolysis cells and the like. In such uses, the polymers are generally used as the layer of a membrane laminate. Multi-layer laminates suffer from delamination under certain operating conditions.

U.S. Patent No. 4,469,744 to Grot et al. uses such polymers in a protective clothing of fabric containing a layer of the highly fluorinated ion-exchange polymer. Example 1 refers to a microporous polytetrafluoroethylene
20 film having a thickness of 127 micrometers as described by U.S. Patent No. 3,962,153. A solution of ion-exchange polymer is applied with the use of a vacuum. The film was then placed in an oven (under vacuum) at 120°C for 5 hours. The final product had a thickness of about 127 micrometers (5 mils) and
25 required the use of a vacuum to provide for impregnation of polymer.

U.S. Patent No. 4,902,308 to Mallouk, et al. relates to a film of porous expanded PTFE having its surfaces, both exterior and internal, coated with a metal salt of perfluoro-cation exchange polymer. The base film of porous, expanded PTFE (ePTFE) had a thickness of between 1 mil and 6 mils (0.025-
30 0.150 mm). The final composite product had a thickness of at least 1 mil (0.025 mm) and preferably had a thickness of between 1.7 and 3 mils (0.043-0.075 mm). The composite product was permeable to air and the air flow, as measured by the Gurley densometer ASTM D726-58, was found to be between
12 and 22 seconds. Therefore, this structure allows fluid to pass through.

U.S. Patent No. 4,954,388 to Mallouk, et al. relates to an abrasion-resistant, tear resistant, multi-layer composite membrane having a film of continuous ion-exchange polymer attached to a reinforcing fabric by means of
35 an interlayer of porous expanded PTFE. A coating of a ion-exchange resin is

present on at least a portion of the internal and external surfaces of the fabric and porous expanded PTFE. The composite membrane made in accordance with the teachings of this patent resulted in thicknesses of greater than 1 mil (0.025 mm) even when the interlayer of porous expanded PTFE had a
5 thickness of less than 1 mil (0.025 mm).

U.S. Patent No. 5,082,472 to Mallouk, et al. relates to a composite membrane of microporous film in laminar contact with a continuous ion-exchange resin layer wherein both layers have similar area dimensions. Surfaces of internal nodes and fibrils of porous expanded (ePTFE) may be
10 coated at least in part with ion-exchange resin coating. The membrane of ePTFE can have a thickness of about 2 mils (0.050 mm) or less and the ion-exchange layer can have a thickness of about 2 mil. The ePTFE layer of this composite membrane imparted mechanical strength to the composite structure. While the patent says the pores can be filled with ion-exchange resin, they
15 cannot be filled to the point where flow of fluids is blocked.

U.S. Patent Nos. 5,094,895 and 5,183,545 to Branca, et al. relate to a composite porous liquid-permeable article having multiple layers of porous ePTFE bonded together and having interior and exterior surfaces coated with an ion-exchange polymer. This composite porous article is particularly useful
20 as a diaphragm in electrolytic cells. The composite articles are described to be relatively thick, preferably between from 0.76 and 5 mm.

U.S. Patent 5,547,551, filed March 15, 1995 to Bahar, et al., describe exchange membrane of expanded porous PTFE less than 0.025mm (25 micron) in which the pores are fully impregnated with an ion-exchange material.
25

Japanese Patent Application No. 62-240627 and Japanese Patent 5-75835 relate to a coated or an impregnated membrane formed with a perfluoro type ion-exchange resin and porous PTFE film to form an integral unit. The resulting composite is not fully occluded with resin since the patent speaks only of thorough impregnation of resin solution.
30

None of the above described materials adequately address the current and anticipated demands for an ion-exchange membrane. There remains a distinct need for a strong, ultra-thin, integral composite ion-exchange membrane, having long term chemical and mechanical stability, very high ionic conductance.
35

SUMMARY OF THE INVENTION

5 The present invention provides thin multi-layer composite membranes of ionic conductance substantially higher than other ion-exchange composite membranes.

The present invention provides a distinct advancement over presently known ion-exchange composite membranes, and the techniques for making such membranes. In one embodiment of the present invention, this is accomplished by a thin integral composite membrane comprised of a microporous polymer 10 film, such as expanded polytetrafluoroethylene having a porous microstructure defined by polymeric fibrils, which provides a reinforcing support that supports an ion-exchange polymer resin impregnated throughout the pores of the porous polymeric film. The micropores of the polymer film extend from one side to the other.

15 The ion-exchange resin can be cationic or anionic. The resin can contain carboxylic functionality or sulfonic functionality; or, both. It can contain phosphonic functionality or sulfonimide functionality. The higher the equivalent weight, the more resistant to anion ion migration. In addition, the ion-exchange resin can contain a filler material that influences passage of chemical moieties.

20 The ion-exchange resin material penetrates into the pores of the microporous polymeric film and occludes all the pore volume of the polymeric film. Thus, the resulting composite is bulk-fluid impermeable and free of pinholes. It will have a Gurley number greater than 10,000.

In some instance, the ion-exchange polymer resin materials will have its 25 functional groups substantially all carboxylic groups ($-\text{COOM}$ where M is H^+ or a metal cation, Na^+ , K^+ , or NH_4^+). In other instances, the ion-exchange polymer resin material will have functional groups that are substantially all sulfonic groups ($-\text{SO}_3\text{M}$ where M is H^+ or a metal cation (Na^+ , K^+ , or NH_4^+)). The ion-exchange resin materials stop or prevent passage of certain anions. 30 To some extent, the sulfonic ion-exchange resin material allows passage of cations, such as Na^+ . They retard passage of OH^- ions, but the carboxylic resins are better in this respect.

The ion-exchange resin materials include such well known materials as fluorinated or nonfluorinated polystyrene sulfonates and sulfonated PTFE. 35 They are preferably fluorinated and more preferably perfluorinated; and preferably are resins containing a sulfonic acid moiety or a carboxylic acid moiety. They can also be ionic polymers derived from polyvinyl alcohol (PVA), styrene-based polymers. To make ion-exchange resins of these, the PVA can

be mixed with a metal salt. The DVB/styrene can be sulfonated. Copolymers of trifluorostyrene and trifluoromethyl trifluorostyrene or similar comonomers which have been sulfonated can be used.

5 The composite membrane formed by the ion-exchange resins and the porous polymer substrate may be bonded to a reinforcement backing of a woven or nonwoven material.

In one embodiment of the present invention, the microporous polymeric film comprises a material having a porous microstructure defined substantially of nodes interconnected with fibrils, such as expanded porous
10 polytetrafluoroethylene. The composite is essentially air impermeable.

A method for making an ion-exchange membrane of the present invention is provided which comprises the following steps:

- (a) providing a membrane having a porous microstructure, preferably with a thickness of less than 0.05 millimeters (50 micron).
- 15 (b) impregnating the membrane with an ion-exchange material so as to render the membrane essentially air impermeable; and
- (c) optionally, heating said impregnated membrane to an elevated temperature above 60°C for a predetermined period of time.

20 The foregoing and other aspects will become apparent from the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

25 A composite membrane is provided which is comprised of microporous polymer film and ion-exchange resin material embedded in and substantially fully occluding the pores of the microporous film.

The embedding of the resin into film improves the adhesion between the two. By employing microporous structures, thin composites can be obtained which provide improved migration of chemical substances through the
30 composites.

The Microporous Polymeric Films

35 Suitable microporous polymer films include those made from polyolefins, polyamides, polycarbonates, cellulose, polyurethanes, polyesters, polyethers, polyacrylates, copolyether esters, copolyether amides, chitosan, and fluoropolymers. Suitable fluoropolymers include membranes of porous polytetrafluoroethylene, more preferably a membrane of expanded porous

PTFE (sometimes referred to as ePTFE) produced by the process taught in U.S. Patent No. 3,953,566 (to Gore).

5 Microporous films of other polymers such as thermoplastic polymers are described in U.S. Patent No. 4,539,256 to Sherman, incorporated herein by reference. Preparation of microporous polyurethanes is described in U.S. Patent No. 4,429,000. Preparation of microporous polymeric films, especially microporous polyolefins (polyethylene, polypropylene, butenes, pentenes, etc.) is described in British Patent 1339207. Preparation of microporous films by stretching is described in U.S. Patent No. 4,726,989 where use of polyamides, 10 polyolefins, polystyrenes, polyvinylidene fluoride, and polycaprolactanes are described. Preparation of microporous films by liquid extraction is described in U.K. Publication No. GB 2,026,381. Teaching is described in U.S. Patent No. 4,100,238. Preparation by film fracture, hot stretching is described in U.S. Patent No. 3,679,540. But these patents are incorporated by reference.

15 To amplify, U.K. Publication No. GB 2,026,381 discloses the preparation of membranes having a porous surface by blending polymer with a liquid component to form a binary two-phase system which, in the liquid aggregate state, has a region of miscibility and a region with miscibility gaps, forming a sheet of the blend, casting the film into a bath of the liquid component and 20 removing the liquid component to provide porosity. The resultant non-oriented porous sheet has a relatively low tensile strength.

U.S. Patent Nos. 3,953,566, 3,962,153, 4,096,227, 4,110,392, 4,187,390 and 4,194,041, all incorporated by reference, describe the preparations of porous articles, including microporous sheets, formed of 25 polytetrafluoroethylene (PTFE), a non-thermoplastic polymer, which is characterized by having a microstructure of nodes connected by fibrils. Such articles are produced by extruding a paste comprised of PTFE particles and a lubricant, removing the lubricant and stretching and annealing the resultant product. The resultant product is a sintered, oriented porous film of PTFE.

30 U.S. Patent Nos. 4,100,238 and 4,197,148, all incorporated by reference, describe the preparation of microporous films by extruding a two component blend, solvent leaching one dispersed component and stretching the resultant leached film to obtain a desired porosity. The blend consists of polymer and a leachable, non-miscible substance. Once the leachable dispersed polymer 35 phase is removed and the film oriented, a porous film results.

U.S. Patent No. 3,679,540, incorporated by reference, discloses a method for making a microporous polymer film by cold stretching an elastic polymer film until porous surface regions are formed by film failure, hot

stretching the cold stretched film until fibrils and pores or open cells are formed and then heat setting the resultant film. Controlled porosity is generally not attained in such films because they do not always uniformly fibrillate to a specific pore size.

5 Certain U.S. patents disclose the preparation of porous polymer film by blending into the polymer non-miscible leachable particulate substance such as starch, salts, etc., forming a sheet and leaching the particulate substance from the polymer sheet. Such U.S. Patents, incorporated by reference, include: U S Patent Nos. 3,214,501 and 3,640,829, U.S. Patent No. 3,870,593
10 discloses the preparation of a microporous polymer sheet by blending non-miscible, non-leachable filler into the polymer, forming a sheet of the blend and stretching the sheet to form pores which are initiated at the sites of the filler particles

 U S Patent No. 4,539,256 which patent is hereby incorporated by
15 reference, teaches a method of making a microporous sheet which comprises the steps of melt blending a crystallizable thermoplastic polymer with a compound which is miscible with the thermoplastic polymer at the polymer melting temperature but immiscible on cooling below the polymer melting temperature, forming a sheet of the melt blend, cooling the sheet to a
20 temperature at which the compound becomes immiscible with the polymer to cause phase separation between the thermoplastic polymer and the compound to provide a sheet.

 Such porous polymer films or sheets will preferably have a porosity of greater than 35%. More preferably, the porosity should be between 70-95%.
25 The thickness of the film is preferably less than 2 mil (0.05 mm, 50 micrometers). Preferably the thickness is between 0.06 mils (1.5 μ m) and 1.6 mils (0.04 mm), and most preferably the thickness is between 0.50 mils (0.013 mm) and 1.50 mils (0.038 mm).

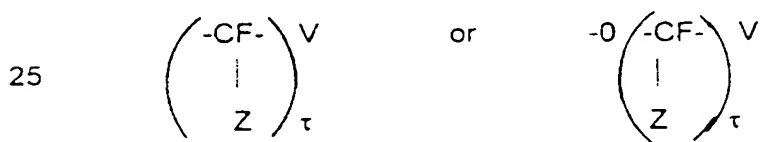
 A preferred film is expanded porous PTFE commercially available in a
30 variety of forms from W. L. Gore & Associates, Inc., under the trademark GORE-TEX® membrane. The porous microstructure of such expanded porous PTFE films either comprises nodes interconnected by fibrils, or comprises substantially fibrils with substantially no nodes present. Preferred porous expanded PTFE films can be characterized as having a bubble point between
35 10 and 60 psi; and an air flow between 20 Frazier and 10 Gurley seconds. It may also have a pore size distribution value between 1.05 and 1.20; and a ball burst strength between 0.9 and 17 pounds/force.

The Ion-exchange Polymeric Resins

The ion-exchange polymeric materials used can be any ion-exchange materials that will provide the desired result. The materials are preferably fluorinated because the material should be substantially inert to chemical activity and should be heat resistant.

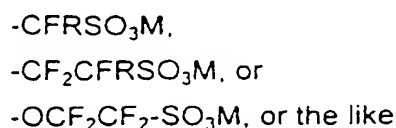
The ion-exchange polymeric material will of course contain ionic functionality, preferably sulfonic or carboxylic moieties. The functional groups are present in an amount sufficient to impart ion-exchange properties to the polymer. An equivalent weight too high it results in the electrical resistivity being too high. But if the equivalent weight is too low, mechanical strength becomes poor. The ionic functionality will usually be provided by carboxylic, sulfonic or phosphonic groups present either on the polymer backbone or present on pendant groups that extend from the polymer backbone in a recurring fashion. The polymer backbone will preferably be a fluorinated hydrocarbon backbone chain. The functional group preferably will have the structure $-\text{COOM}$, $-\text{SO}_3\text{M}$ or PO_3M_2 , where M is hydrogen, a metallic cation or NH_4^+ . If a metallic cation, it will preferably be an alkali metal or an alkaline earth metal, such as Na^+ , K^+ or the like.

For carboxylic functionality, the pendant side chains which carry the above functional groups may have at the terminal end of the side chain a group of the formula:



where V is $-\text{COOM}$, Z is $-\text{F}$ or $-\text{CF}_3$ and τ is an integer of 1-12, preferably 1 or 2, as described in U.S. Patent 4,437,951 to DuPont, all of which is incorporated by reference for its disclosure of both carboxylic and sulfonic functionality.

The sulfonyl polymers with which the present invention is concerned are typically polymers having a fluorinated hydrocarbon backbone chain to which are attached the sulfonic containing functional groups as pendant side chains. For sulfonic polymers, the terminal portion of side chains can be:



where R is F, Cl, or perfluoroalkyl and M is as described earlier.

For phosphoric polymers, the same sort of pendant groups are present.

Other ion-exchange resins useful herein, in addition to the fluorinated
5 carboxylic resins and the fluorinated sulphonic and phosphoric resins described
above, include, but are not limited to, polyvinyl alcohol (PVA), divinyl
benzene/styrene copolymers, provided they have the requisite functional
groups, or pendant chains. The polymers can be mixed with a metal salt to
obtain the desired functionality. A sulfonated polymer of trifluorostyrene such
10 as homopolymer or a copolymer with tetrafluoroethylene can be used.

It is understood that the foregoing description of ion-exchange resins is not
limiting and is only representative. The invention can employ any type of ion-
exchange material. Thus, as seen above, not only do the resins include ones
with the functional group, a part of the polymer, ones where the functional
15 group are provided by an additive to the polymer.

The ion-exchange resins used in the present invention can be prepared by
general polymerization techniques developed for homo and copolymerizations
of fluorinated ethylenes, particularly those employed for tetrafluoroethylene
which are described in the literature. Nonaqueous techniques for preparing the
20 copolymers include that of U.S. Patent No. 3,041,317, that is, by the
polymerization of a mixture of the major monomer therein, such as
tetrafluoroethylene, and a fluorinated ethylene containing a sulfonyl fluoride
group in the presence of a free radical initiator, preferably a perfluorocarbon
peroxide or azo compound, at a temperature in the range 0°-200°C. and at
25 pressures in the range of 10^5 to 2×10^7 pascals (1-200 Atm.) or higher. The
nonaqueous polymerization may, if desired, be carried out in the presence of a
fluorinated solvent. Suitable fluorinated solvents are inert, liquid, perfluorinated
hydrocarbons, such as perfluormethylcyclohexane,
perfluorodimethylcyclobutane, perfluorooctane, perfluorobenzene and the like,
30 and inert, liquid chloro-fluorocarbons such as 1,1,2-trichloro-1,2,2-
trifluoroethane, and the like. Aqueous techniques for preparing such
copolymers include contacting the monomers with an aqueous medium
containing a free-radical initiator to obtain a slurry of polymer particles in non-
water-wet or granular form, as disclosed in U.S. Patent No. 2,393,967, or
35 contacting the monomers with an aqueous medium containing both a free -
radical initiator and a telogenically inactive dispersing agent, to obtain an
aqueous colloidal dispersion of polymer particles, and coagulating the

dispersion, as disclosed, for example, in U.S. Patent No. 2,559,752 and U.S. Patent No. 2,593,583.

In addition, ion-exchange polymer resins described and prepared as in U.S. Patent Nos. 4,267,364 to DuPont; 4,544,458 to DuPont; 4,178,218 to Asahi; 4,255,523 to Asahi; 5,082,472 to Mallouk, et al.; and 5,422,411 to Wei, all incorporated by reference, can be used.

Optionally, the ion-exchange resin materials may be complemented by containing finely divided powders or other non-ionic polymers to provide final composites. Such a finely divided powder may be selected from a wide range of organic and inorganic compounds such as, but not limited to, a metal oxide, carbon black, graphite, nickel, silica, titanium dioxide, platinum black, for example, to provide specific added effects such as different aesthetic appearance (color), electrical conductivity, thermal conductivity, catalytic effects, or enhanced or reduced reactant transport properties. Examples of non-ionic polymers include, but are not limited to, polyolefins, other fluoropolymers such as polyvinylidene fluoride (PVDF), or other thermoplastics and thermoset resins. Such non-ionic polymers may be added to aid occlusion of the substrate matrix, or to enhance or reduce reactant transport properties.

Preparation of the Composites of the Invention

Composites of the invention can conveniently be prepared using a precursor ion-exchange polymer, which is in a form that makes it thermoplastic. Thus, in one approach, ion-exchange resin in its melt-processible or other precursor polymer is completely embedded in the pores of the microporous polymeric film support material. It was found, surprisingly, that at temperatures in excess of 290° C the forces of gravity and capillary action are usually sufficient to achieve this purpose without the use of any additional force or pressure. Accordingly, a sheet of microporous support material can be placed on a suitable sheet of release agent, such as aluminum foil, in an oven, covered with a film of precursor polymer and heated to 290 to 340° C for a period of 5 to 25 minutes. On the other hand, instead of resting on the release agent, the sheet of support material may also be freely suspended in the oven in a horizontal position. In either case, the process can also be performed continuously by passing the components in contact with each other through an oven or heated zone; for instance radiant heat or microwave radiation. The pores can be embedded from one side to the other, or the composite can be turned over and the resin applied to the other side by the same technique.

The resulting composite can then be immersed in a hot solution of sodium or potassium hydroxide in order to convert the precursor polymer to its ionic sodium or potassium salt form. The time required for this conversion depends on the temperature and concentration of the caustic solution; 60 minutes at 90°
5 C in a 10% solution of sodium hydroxide would be a typical value. It is known that the addition of solvents such as dimethylsulfoxide will speed up this reaction

In another method, a support structure, such as a polypropylene woven fabric, or a ePTFE woven fabric may first be laminated to the untreated porous
10 polymer film by any conventional technique, such as, hot roll lamination, ultrasonic lamination, adhesive lamination, or forced hot air lamination so long as the technique does not damage the integrity of the base material. Alternatively, a liquid composition can be prepared containing an ion-exchange resin material in solvents such as methanol, isopropanol, dimethylformamide or
15 dimethyl sulfoxide. Solvents that are suitable for use include, for example, alcohols, carbonates, THF (tetrahydrofuran), water, and combinations thereof. The liquid compositions may be applied to the porous film by any conventional coating technique including forwarding roll coating, reverse roll coating, gravure coating, doctor coating, kiss coating, as well as dipping, brushing, painting, and
20 spraying so long as the liquid solution is able to penetrate the interstices and interior volume of the film. Excess liquid composition from the surface of the film may be removed. The treated film is then immediately placed into an oven to dry. For the polypropylene fabric, oven temperatures may range from 60-200°C, but preferably 120-160°C can be used. Drying the treated membrane
25 in the oven causes the ion-exchange resin material to become securely adhered to both the external and internal membrane surface, i.e., the fibrils and/or nodes of the porous PTFE polymer.

Additional liquid composition application steps, and subsequent drying, may be repeated. The material is turned over and the second ion-exchange
30 resin material supplied to the other surface of the material. Typically, several treatments are needed, but the actual number of treatments is dependent on the ionomer concentration and thickness of the membrane.

Alternatively, no woven fabric need be used for the porous polymer film can be treated alone, without any supporting fabric present.

35

The Composites

The composite membrane has excellent long term chemical stability.

Because the composite membrane of the present invention can be made
5 thinner than a fabric or non-woven reinforced structure, it is possible to transport ions with lower resistance than previously has been achieved.

The composite membrane of the present invention is uniform and mechanically strong. As used herein, the term "uniform" is defined as continuous impregnation with the ion-exchange material such that no pin holes
10 or other discontinuities exist within the composite structure. The membrane should be "occlusive", meaning that the interior volume of the porous membrane is impregnated such that the interior volume is substantially filled with the ion-exchange material and the final membrane is essentially air impermeable, having a Gurley number of greater than 10,000 seconds.

15 The composite membrane of the present invention may be employed in various applications, including but not limited to, polarity-based chemical separations; electrolysis; fuel cells and batteries; pervaporation; gas separation; dialysis separation; industrial electrochemistry, such as chloralkali production and other electrochemical applications.

20 The final composite membrane of the present invention has a uniform thickness free of any discontinuities or pinholes on the surface. The interior volume of the membrane is occluded such that the composite membrane is impermeable to non-polar gases and to bulk flow of liquids.

Optionally, the composite membrane may be reinforced with a woven or
25 non-woven material. Suitable woven materials may include, for example, scrims made of woven fibers of expanded porous polytetrafluoroethylene; webs made of extruded or oriented polypropylene or polypropylene netting, commercially available from Conwed, Ind. of Minneapolis, MN; and woven materials of polypropylene and polyester, from Tetko, Inc., of Briarcliff Manor,
30 New York. Suitable non-woven materials may include, for example, a spun-bonded polypropylene from Reemay, Inc. of Old Hickory, TN.

One of the uses of the composite ion-exchange membrane of the invention is in electrochemical cells. Such a cell comprises an anode, a compartment for the anode, a cathode, a compartment for the cathode, and a membrane which
35 is situated to separate the two said compartments. One example is a chloralkali cell, for which the membrane should have the functional groups in salt form; in such a cell, a layer of the membrane which has carboxylic functional groups will be disposed toward the cathode compartment.

The electrochemical cell, especially a chloralkali cell, will ordinarily be constructed such that the gap or spacing between the anode and cathode is narrow, i.e., no greater than about 3 mm. It is also often advantageous to operate the cell and electrolysis process with the membrane in contact with either the anode or cathode, which can be accomplished with the aid of an appropriate hydraulic head in one cell compartment, or by using an open mesh or grid separator to urge the membrane and selected electrode into contact. It is often further advantageous for the membrane to be in contact with both the anode and cathode in an arrangement referred to as a zero-gap configuration. Such arrangements offer advantages in minimizing the resistance contributed by the anolyte and catholyte, and thus provide for operation at low voltage. Whether or not such arrangements are used, either or both electrodes can have an appropriate catalytically active surface layer of type known in the art for lowering the overvoltage at an electrode.

When used in a film or membrane to separate the anode and cathode compartments of an electrolysis cell, such as a chloralkali cell, the perfluorosulfonate polymers dealt with herein, after conversion to ionizable form, should have a total ion-exchange capacity of 0.5 to 3.3 meq/g (milliequivalents/gram), preferably at least 0.6 meq/g, and more preferably from 0.8 to 2.5 meq/g. Below an ion-exchange capacity of 0.5 meq/g, the electrical resistivity becomes too high, and above 3.3 meq/g the mechanical and electrochemical properties are poor because of excessive swelling of the polymer. The relative amounts of the comonomers which make up the polymer should be adjusted or chosen such that the polymer has an equivalent weight no greater than about 2000, preferably no greater than about 1600, although lower values such as 1400 or less can be used for use as an ion-exchange barrier in an electrolytic cell. The equivalent weight above which the resistance of a film or membrane becomes too high for practical use in an electrolytic cell varies somewhat with the thickness of the film or membrane. For thinner films and membranes, equivalent weights up to about 2000 can be tolerated. Ordinarily, the equivalent weight will be at least 300, and preferably at least 500. Film of polymer having sulfonyl groups in ion-exchange form preferably will have an equivalent weight no greater than 1500 or 1600.

For the carboxylate polymers dealt with herein, when used to separate the compartments of a chloralkali cell, the requirements in respect to the ion-exchange capacity thereof differ from those of the sulfonate polymers. The carboxylate polymer should have an ion-exchange capacity of at least 0.6 meq/g, preferably at least 0.7 meq/g, and most preferably at least 0.8 meq/g, so

as to have acceptably low resistance. Such values are especially applicable in the case of films having a thickness in the lower end of the specified thickness range of 10 to 100 microns; for films in the middle and upper end of this range, the ion-exchange capacity should be at least 0.7 meq/g and preferably at least 0.8 meq/g. The ion-exchange capacity should be no greater than 2.5, preferably no greater than 2 meq/g, more preferably no greater than 1.8 or 1.5 meq/g, and more preferably no greater than 1.3 meq/g. In terms of equivalent weight, the carboxylate polymer most preferably has an equivalent weight in the range of 550 or 770 to 1250.

10 The membranes described herein can be used as a substrate to carry an electrocatalyst composition on either surface or both surfaces thereof, the resulting article being a composite membrane/electrode assembly. The thickness of the composites can be 5 mils or less.

Such electrocatalyst can be of a type known in the art, such as those described in U.S. Patent Nos. 4,224,121 and 3,134,697, and published UK Patent Application No. GB 2,009,788A. Preferred cathodic electrocatalysts include platinum ones, such as platinum black, platinum on carbon black, Raney nickel and ruthenium black. Preferred anodic electrocatalysts include tungsten oxide, platinum black, platinum on carbon black, mixed ruthenium and iridium oxides, or platinum-ruthenium alloys.

20 The membranes described herein can also be modified on either surface or both surfaces thereof so as to have enhanced gas release properties, for example by providing optimum surface roughness or smoothness, or, preferably, by providing thereon a gas and liquid permeable porous non-electrode layer or a nonporous ion-permeable, hydrophilic layer. Such non-electrode layer should have a porosity of 10 to 99%, preferably 30 to 70%, and an average pore diameter of 0.01 to 2000 microns, preferably 0.1 to 1000 microns, and a thickness generally in the range of 0.1 to 500 microns, preferably 1 to 300 microns. a non-electrode layer ordinarily comprises an inorganic component and a binder; the inorganic component can be of a type as set forth in published UK Patent Application No. GB 2,064,586A, preferably tin oxide, titanium oxide, zirconium oxide, or an iron oxide such as Fe_2O_3 or Fe_3O_4 . Other information regarding non-electrode layers on ion-exchange membranes is found in published European patent Application No. 0,031,660, and in Japanese Laid-open patent Applications Nos. 56,108888 and 56,112487.

35 The binder component in a non-electrode layer, and in an electrocatalyst composition layer, can be, for example, polytetrafluoroethylene, a fluorocarbon

polymer at least the surface of which is hydrophilic by virtue of treatment with ionizing radiation in air or a modifying agent to introduce functional groups such as --COOH or --SO₃H (as described in published UK Patent Application No. GB 2,060,703A) or treatment with an agent such as sodium in liquid ammonia, a
5 functionally substituted fluorocarbon polymer or copolymer which has carboxylate or sulfonate functional groups, or polytetrafluoroethylene particles modified on their surfaces with fluorinated copolymer having acid type functional groups (No. GB 2,064,586A). Such binder is suitably used in an amount of 10 to 50% by wt. of the non-electrode layer or of the electrocatalyst
10 composition layer.

Composite structures having non-electrode layers and/or electrocatalyst composition layers thereon can be made by various techniques known in the art, which include preparation of a decal which is then pressed onto the membrane surface, application of a slurry in a liquid composition (e.g.,
15 dispersion or solution) of the binder followed by drying, screen or gravure printing of compositions in past form, hot pressing of powders distributed on the membrane surface, and other methods as set forth in No. GB 2,064,586A. Such structures can be made by applying the indicated layers onto membranes in melt-fabricable form, and by some of the methods onto membranes in ion-
20 exchange form; the polymeric component of the resulting structures when in melt-fabricable form can be hydrolyzed in known manner to the ion-exchange form.

Non-electrode layers and electrocatalyst composition layers can be used in combination in various ways on a membrane. For example, a surface of the
25 membrane can be modified with a non-electrode layer, and an electrocatalyst composition layer disposed over the latter. It is also possible to place on a membrane a layer containing both an electrocatalyst and a conductive non-electrode material, e.g. metal powder which has a higher over-voltage than the electrocatalyst, combined into a single layer with a binder. One preferred type
30 of membrane is that which carries a cathodic electrocatalyst composition on one surface thereof, and a non-electrode layer on the opposite surface thereof.

Membranes which carry thereon one or more electrocatalyst layers, or one or more non-electrode layers, or combinations thereof, can be employed in an electrochemical cell in a narrow-gap or zero-gap configuration as described
35 above.

The following testing procedures were employed on samples which were prepared in accordance with the teachings of the present invention.

TEST PROCEDURES

Tensile Test

5 Tensile tests were carried out on an Instron Model 1122 tensile strength tester, in accordance with ASTM D 638-91. Machine parameters were set as follows:

Cross head speed (in/min): 0.423 cm/sec.

Full Scale load range (lbs): 222.4 N

10 Humidity (%): 50

Temperature (deg F): 22.8°C

Grip Distance: 6.35 cm

Specimens were stamped out to conform with Type (II) of ASTM D638. The specimens had a width of 0.635 cm, and a gauge length of 2.54 cm.

15

Thickness

Thickness of the base material was determined with the use of a snap gauge (Johannes Kafer Co. Model No. F1000/302). Measurements were taken
20 in at least four areas of each specimen. Thickness of the dried composite membrane was also obtained with the use of the snap gauge. Thicknesses of swollen samples were not measurable with the snap gauge due to the compression or residual water on the surface of the swollen membrane. Thickness measurements of the swollen membranes were also not able to be
25 obtained with the use of scanning electron microscopy due to interferences with the swelling agents.

Moisture Vapor Transmission Rate (MVTR)

30 A potassium acetate solution, having a paste like consistency, was prepared from potassium acetate and distilled water. (Such a paste may be obtained by combining 230 g potassium acetate with 100 g of water, for example.) This solution was placed into a 133 ml. polypropylene cup, having an inside diameter of 6.5 cm. at its mouth. An expanded
35 polytetrafluoroethylene (ePTFE) membrane was provided having a minimum MVTR of approximately 85,000 g/m²-24 hr as tested by the method described in U.S. Patent No. 4,862,730 to Crosby. The ePTFE was heat sealed to the lip

of the cup to create a taut, leakproof, microporous barrier containing the solution.

A similar ePTFE membrane was mounted to the surface of a water bath. The water bath assembly was controlled at $23^{\circ}\text{C} \pm$ plus or minus 0.2°C ,
5 utilizing a temperature controlled room and a water circulating bath.

Prior to performing the MVTR test procedure, a sample to be tested was allowed to condition at a temperature of 23°C and a relative humidity of 50%. The sample to be tested was placed directly on the ePTFE membrane mounted to the surface of the water bath and allowed to equilibrate for 15 minutes prior
10 to the introduction of the cup assembly.

The cup assembly was weighed to the nearest 1/1000g. and was placed in an inverted manner onto the center of the test sample.

Water transport was provided by a driving force defined by the difference in relative humidity existing between the water in the water bath and the
15 saturated salt solution of the inverted cup assembly. The sample was tested for 10 minutes and the cup assembly was then removed and weighed again within 1/1000g.

The MVTR of the sample was calculated from the weight gain of the cup assembly and was expressed in grams of water per square meter of sample
20 surface area per 24 hours.

Peel Strength

Peel strength or membrane adhesion strength tests were conducted on
25 membrane samples prepared with reinforced backings. Test samples were prepared having dimensions of 3 inches by 3.5 inches (7.62 cm x 8.89cm). Double coated vinyl tape (type - #419 available from the 3M Company of Saint Paul, Minnesota) having a width of 1 inch (2.54 cm) was placed over the edges of a 4 inch by 4 inch (10.2 cm x 10.2 cm) chrome steel plate so that tape
30 covered all edges of the plate. The membrane sample was then mounted on top of the adhesive exposed side of the tape and pressure was applied so that sample was adhesively secured to the chrome plate.

The plate and sample were then installed, in a horizontal position, within an Instron tensile test machine Model No. 1000. An upper crosshead of the
35 tensile test machine was lowered so that the jaws of the test machine closed flat and tightly upon the sample. The upper crosshead was then slowly raised pulling the membrane sample from the reinforced backing. When the membrane detached from the reinforced backing, the test was complete.

Adhesion strength was estimated from the average strength needed to pull the membrane from the reinforced backing.

Ionic Conductance

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The ionic conductance of the membrane was tested using a Palico 9100-2 type test system. This test system consisted of a bath of 1 molar sulfuric acid maintained at a constant temperature of 25°C. Submerged in the bath were four probes used for imposing current and measuring voltage by a standard "Kelvin" four-terminal measurement technique. A device capable of holding a separator, such as the sample membrane to be tested, was located between the probes. First, a square wave current signal was introduced into the bath, without a separator in place, and the resulting square wave voltage was measured. This provided an indication of the resistance of the acid bath. The sample membrane was then placed in the membrane-holding device, and a second square wave current signal was introduced into the bath. The resulting square wave voltage was measured between the probes. This was a measurement of the resistance due to the membrane and the bath. By subtracting this number from the first, the resistance due to the membrane alone was found.

Dimensional Stability

Reverse expansion in the x and y direction upon dehydration was measured using a type Thermomechanical Analyzer 2940, made by TA Instruments, Inc., of New Castle, DE. This instrument was used to apply a predetermined force to a sample that had been boiled in water for 30 minutes. A quartz probe placed in contact with the sample measured any linear changes in the sample as it dried. A sample was placed in a holder and then dried at 75°C for greater than 10 min. The change in dimension (i.e., the shrinkage) was recorded as a percentage of the original weight.

Weight-Loss With Temperature

A high resolution TGA 2950, Thermogravimetric Analyzer, made by TA Instruments (Newcastle, DE) was used to determine the weight loss of samples with respect to temperature. This weight loss is an indication of the water content of the ionomer sample. Samples were heated at a rate of 10°C/min up

to a temperature of 150°C, and the weight loss was recorded as a percentage of the original weight @ 100°C as follows:

Bubble Point Test

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Liquids with surface free energies less than that of stretched porous PTFE can be forced out of the structure with the application of a differential pressure. This clearing will occur from the largest passageways first. A passageway is then created through which bulk air flow can take place. The air flow appears as a steady stream of small bubbles through the liquid layer on top of the sample. The pressure at which the first bulk air flow takes place is called the bubble point and is dependent on the surface tension of the test fluid and the size of the largest opening. The bubble point can be used as a relative measure of the structure of a membrane and is often correlated with some other type of performance criteria, such as filtration efficiency.

10

The Bubble Point was measured according to the procedures of ASTM F316-86. Isopropyl alcohol was used as the wetting fluid to fill the pores of the test specimen.

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The Bubble Point is the pressure of air required to displace the isopropyl alcohol from the largest pores of the test specimen and create the first continuous stream of bubbles detectable by their rise through a layer of isopropyl alcohol covering the porous media. This measurement provides an estimation of maximum pore size.

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Pore Size and Pore Size Distribution

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Pore size measurements are made by the Coulter Porometer™, manufactured by Coulter Electronics, Inc., Hialeah, FL. The Coulter Porometer is an instrument that provides automated measurement of pore size distributions in porous media using the liquid displacement method (described in ASTM Standard E1298-89). The Porometer determines the pore size distribution of a sample by increasing air pressure on the sample and measuring the resulting flow. This distribution is a measure of the degree of uniformity of the membrane (i.e., a narrow distribution means there is little difference between the smallest and largest pore size). The Porometer also calculates the mean flow pore size. By definition, half of the fluid flow through the filter occurs through pores that are above or below this size. It is the mean flow pore size which is most often linked to other filter properties, such as

30

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retention of particulates in a liquid stream. The maximum pore size is often linked to the Bubble Point because bulk air flow is first seen through the largest pore.

5 Ball Burst Test

 This test measures the relative strength of a sample by determining the maximum load at break. The sample is challenged with a 1 inch diameter ball while being clamped between two plates. The material is placed taut in the
10 measuring device and pressure applied with the ball burst probe. Pressure at break is recorded.

Air Flow Data

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15 The Gurley air flow test measures the time in seconds for 100cc of air to flow through a one square inch sample at 4.88 inches of water pressure. The sample is measured in a Gurley Densometer (ASTM 0726-58). The sample is placed between the clamp plates. The cylinder is then dropped gently. The automatic timer (or stopwatch) is used to record the time (seconds) required for
20 a specific volume recited above to be displaced by the cylinder. This time is the Gurley number.

 The Frazier air flow test is similar but is mostly used for much thinner or open membranes. The test reports flow in cubic feet per minute per square foot of material at 0.5 inches water pressure. Air flow can also be measured
25 with the Coulter Porometer. In this test, the operator can select any pressure over a wide range. The Porometer can also perform a pressure hold test that measures air flow during a decreasing pressure curve.

BACKGROUND OF EXAMPLES

30 As may be appreciated by one skilled in the art, the present invention provides for an ultra-thin, integral composite membrane having thicknesses which are significantly less than the thicknesses of conventional multi-layer membranes. As a result, the membranes of the present invention provide
35 lower electrical resistance. Also, because no porous surfaces are exposed in the present invention, there is no propensity for gasses to become trapped within the interior volume of the membrane thereby causing increased electrical resistance.

As described hereinabove, the ultra-thin integral composite membrane of the present invention can be advantageously employed in electrolytic processes and chemical separations. In a plate-and-frame type electro dialysis unit, the membrane of the present invention would take the place of existing cation exchange membranes. This membrane could be of the type which is laminated to a spacer screen in accordance with a specific application. Due to the higher conductance of this membrane, an electro dialysis unit could employ less membrane to achieve a given flux rate, thereby saving space and cost. If equipment is retro-fitted with this membrane, the voltage requirements would be reduced at a given current, or higher current could be run at a given voltage. Also, in a diffusion dialysis system, a given unit employing the membrane of the present invention would provide a higher flux.

A fuel cell, utilizing the membrane of the present invention, operates at a higher voltage for a given current density due to the improved ionic conductance of this membrane.

Also, due to improved water transport across the membrane, high limiting current may be achieved with less fuel gas humidification, as compared to membranes which have been employed heretofore. For example, the membrane of the present invention has a resistance of 0.044 ohm-sq. Cm. At a current density of 1 A/cm² this causes a voltage drop of about 44 mV, or about a 99mV improvement in cell voltage compared to Nafion 117 membranes which have a resistance of 0.143 Ω -cm³. This may reduce losses by about 99 mW/sq cm at this operating condition for resistance. If the cell operating voltage increased from 500 mV to 599 mV, the cell voltage efficiency would increase from 41% to 49% of the theoretical 1.23 V. The decrease in the internal resistance of the cell allows the design of smaller or more efficient cells. All samples of ePTFE provided in the following examples were made in accordance with the teachings of U.S. Patent No. 3,953,566. Representative ePTFE membranes may have the following:

30

	<u>Membrane 1</u>	<u>Membrane 2</u>
Gurley (sec.)	3.3	0.9
Bubble Point (psi)	28.3	32.6
Mass/Area (g/m ²)	6.1	4.4
35 Density (g/cc)	0.65	0.77
Longitudinal Maximum Load (lbs.)	1.76	2.18
Transverse Maximum Load (lbs.)	2.33	1.31
Nominal Pore Size (μ m)	0.2	0.2

As may be appreciated by one skilled in the art, ePTFE membranes can be made with a wide range of physical property values.

Without intending to limit the scope of the present invention, the
5 apparatus and method of production of the present invention may be better understood by referring to the following examples.

Example 1

A sample of expanded microporous polytetrafluoroethylene membrane
10 made in accordance with the teachings of U.S. Patent 3,953,566, was obtained from W L Gore & Associates, Inc. The membrane, with a nominal thickness of 0.75 mils (0.02 mm), was mounted on a 6 inch wooden embroidery hoop. A solution was prepared comprising 95% by volume of a perfluorosulfonic acid/tetrafluoroethylene copolymer resin (in H⁺ form) in a solution of low
15 molecular weight alcohols comprising propanol, butanol, and methanol known as Nafion NR-50 (1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 5% of a nonionic surfactant of octyl phenoxy polyethoxyethanol known as Triton X-100 commercially available from Rohm & Hass of Philadelphia, PA. This solution was brushed on both sides of the
20 membrane so as to impregnate and substantially occlude the micropore structure. The sample was then dried in the oven at 140°C for 30 seconds. The procedure was repeated two more times to fully occlude the micropores. The sample was then soaked in isopropanol for 5 minutes to remove the surfactant. After rinsing with distilled water and allowing to dry at room
25 temperature, a final coat of the Nafion-surfactant solution as described above was applied. The wet membrane was again dried in the oven at 140°C for 30 seconds and soaked in isopropanol for 2 minutes. The membrane was finally boiled in distilled water for 10 minutes under atmospheric pressure to swell the treated membrane. Gurley numbers for this material are summarized in Table
30 3. Ionic conductive rates are summarized in Table 4. The strength modulus is found in Table 5. Percent linear expansion is found in Table 6; and percent weight change of this sample is found in Table 7. The swollen membrane was later dried to a dehydrolyzed state in an oven at 140°C for 30 seconds. The thickness of the dried composite membrane was measured and found to be
35 approximately the same thickness as the base material.

Example 2

A sample of expanded microporous PTFE membrane made in accordance with the teachings of U.S. Patent No. 3,953,566, nominal thickness of 0.75 mils (0.02 mm) and a Gurley Densometer air flow of 2-4 seconds
5 obtained from W. L. Gore & Associates, Inc., was placed on top of a netting of polypropylene obtained from Conwed Plastics Corp. of Minneapolis, MN. The two materials were bonded together on a laminator with 10 psig pressure, a speed of 15 feet per minute and a temperature of 200°C. No adhesives were used. The reinforced membrane sample was then placed on a 6 inch wooden
10 embroidery hoop. A solution of 96% by volume of a perfluorosulfonic acid/TFE copolymer resin in alcohol (Nafion NR-50; 1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 4% of the nonionic surfactant Triton X-100 obtained from Rohm & Haas was prepared. This solution was brushed on the membrane side only to substantially occlude the micropores and the
15 sample was dried in an oven at 130°C. This procedure was repeated three more times to fully occlude the micropores. The sample was then baked in an oven at 140°C for 5 minutes. The sample was soaked in isopropanol for 5 minutes to remove the surfactant. The membrane was then boiled in distilled water for 30 minutes under atmospheric pressure causing the treated
20 membrane to swell. Gurley numbers for this material are summarized in Table 3.

This sample was tested for its peel strength in accordance with the method described above. The linear bond strength was found to be 2.06 lb/sq. in. (1450 kg/m²).

25

Example 3

A sample of expanded porous polytetrafluoroethylene membrane made in accordance with the teachings of U.S. Patent No. 3,953,566, and obtained as above, having a thickness of 0.5 mils (0.01 mm) was mounted on a 6 inch
30 wooden embroidery hoop. A solution of 100% Nafion resin solution, perfluorosulfonic acid/TFE copolymer resin in a solvent mixture of propanol, butanol, and methanol known commercially from E.I. DuPont de Nemours, Inc. as Nafion® solution NR-50 (1100 EW) without the addition of any surfactants was brushed onto both sides of the membrane to substantially occlude the
35 micropores. The sample was then placed in an oven at 160°C to dry. This procedure was repeated four more times until the membrane was completely transparent and the micropores were fully occluded. The sample was then boiled in distilled water for 30 minutes at atmospheric pressure causing the

membrane to swell. Gurley numbers for this material are summarized in Table 3.

Example 4

5 A sample of expanded porous polytetrafluoroethylene membrane obtained as above and made in accordance with the teachings of U.S. Patent No. 3,953,566 having a thickness of 0.5 mils (0.01 mm) was mounted on a 6 inch wooden embroidery hoop. A solution of 99% by volume Nafion NR-50 commercially available from E.I. DuPont de Nemours, Inc. and 1% surfactant
10 mixture was prepared. The surfactant mixture consisted of 50% of a nonionic surfactant, Triton X-100 commercially available from Rohm & Haas Corp. and 50% Zonyl FSO commercially available from E.I. DuPont de Nemours, Inc. This solution was brushed on both sides of the membrane and was allowed to dry at room temperature. This procedure was repeated 4 more times until the
15 sample was completely transparent and the micropores were fully occluded. The sample was not treated so as to remove the surfactant. The composite membrane was boiled in distilled water for 5 minutes causing the membrane to swell. The Gurley number for this material is summarized in Table 3.

20 Example 5

 A sample of expanded porous polytetrafluoroethylene membrane obtained as above and made in accordance with the teachings of U.S. Patent No. 3,953,566 having thickness of 0.5 mils (0.01 mm) was mounted onto a 6 inch wooden embroidery hoop. A solution of 95% by volume Nafion NR-50
25 (1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 5% of a nonionic surfactant, Triton X-100 commercially available from Rohm & Haas was prepared. The solution was brushed on both sides of the membrane with a foam brush and the excess was wiped off. The wet membrane was dried in an oven at 140°C for 30 seconds. Three additional coats of solution
30 were applied to the membrane in the same manner to fully occlude the micropores. The membrane was then soaked in isopropanol for 2 minutes to remove the surfactant. The membrane was rinsed with distilled water and allowed to dry at room temperature. A final treatment of the Nafion-Triton solution was applied. The wet membrane was dried in the oven at 140°C for
35 30 seconds, then soaked in isopropanol for 2 minutes. Finally, the membrane was boiled in distilled water for 5 minutes. Moisture vapor transmission rates for the treated membrane were measured and are summarized in Table 1. The Gurley number of the treated membrane are summarized in Table 3.

Example 6

A sample of expanded porous polytetrafluoroethylene membrane made in accordance with the teachings of U.S. Patent No. 3,953,566 having a nominal thickness of 0.75 mils (0.02 mm). Was mounted onto a 6 inch wooden embroidery hoop. The Gurley Densometer air flow on this membrane was 2-4 seconds. A solution of 95% by volume Nafion NR-50 (1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 5% Triton X-100 nonionic surfactant from Rohm & Haas was prepared. The solution was brushed on both sides of the membrane with a foam brush and the excess was wiped off. The wet membrane was dried in the oven at 140°C for 30 seconds. Three additional coats of solution were applied in the same manner. The membrane was then soaked in isopropanol for 2 minutes. After rinsing with distilled water and allowing to dry at room temperature, a final coat of the Nafion surfactant solution was applied. The wet membrane was dried in the oven at 140°C for 30 seconds, then soaked in isopropanol for 2 minutes. This material was not boiled. No swelling other than the minor swelling during the surfactant removal occurred. The ionic conduction rate for this material is presented in Table 4.

Example 7

A sample of expanded porous polytetrafluoroethylene membrane obtained as above and made in accordance with the teachings of U.S. Patent No. 3,953,566 having a nominal thickness of 0.75 mils (0.02 mm) was mounted onto a 5 inch plastic embroidery hoop. The Gurley densometer air flow on this membrane was 2-4 seconds. A solution of 95% by volume Nafion NR-50 (1100 EW) commercially available from E.I. DuPont de Nemours, Inc. and 5% Triton X-100 nonionic surfactant from Rohm & Haas was prepared. The solution was brushed on both sides of the membrane with a foam brush and the excess was wiped off. The wet membrane was dried in the oven at 140°C for 30 seconds. Two additional coats of solution were applied in the same manner so as to fully occlude the micropores. The membrane was then soaked in isopropanol for 2 minutes. After rinsing with distilled water and allowing to dry at room temperature, a final coat of the same Nafion NR-50 Triton X-100 solution was applied. The wet membrane was dried in the oven at 140°C for 30 seconds and then soaked in isopropanol for 2 minutes to remove the surfactant. The sample was rinsed and dried at room temperature. No boiling occurred.

This sample was weighed before it was mounted on the 5 inch plastic hoop. Following treatment, it was removed from the hoop and weighed again. The ion-exchange polymer content was directly calculated by determining the weight change before and after treatment. The ion-exchange content for this sample was found to be 98.4 mg. Or 9.81 grams per square meter of membrane.

A sample of Nafion 115 (5 mils, 0.13 mm) commercially available from E.I. DuPont de Nemours, Inc. was cut to a 1 inch (25.4 mm) by 1 inch (25.4 mm) sample, weighed and found to be 216 grams per square meter.

Nafion Comparative Samples

Nafion 117, a perfluorosulfonic acid cation exchange membrane, unreinforced film of 1100 equivalent weight commercially available from E.I. DuPont de Nemours, Inc. having a quoted nominal thickness of 7 mils (0.18 mm) was obtained. Samples of it, originally in the hydrated swollen state, were measured in the x- and y-directions and weighed. The samples were then dried in a convection oven at 140°C for approximately 1 minute to an unswollen state and then remeasured from which expansion and weight change measurements found in Tables 6 and 7 were calculated.

Nafion 115, a perfluorosulfonic acid cation exchange membrane, unreinforced film of 1100 equivalent weight also commercially available from E.I. DuPont de Nemours, Inc. having a nominal thickness of 5 mils (0.1 mm) was obtained. This sample was also obtained commercially in the hydrated swollen state. Data on it is found in Tables 4 and 5.

TABLE 1
Moisture Vapor Transmission Rates (MVTR)

Sample ID*	MVTR (grams/m ² -24 hrs.)
Example 5	25.040
Nafion 117	23.608

*Measurements were obtained on samples in their swollen state.

TABLE 2
Tensile Test

Sample ID	(Avg) Normalized Stress @ Max Load (psi)	
	M-Dir	XM-Dir
Example 1	4706	2571
Nafion 117*	2308	1572
Example 6	4988	3463
Nafion 117 **	4314	3581

* sample was boiled in distilled water for 30 minutes.

5 ** sample was tested as received from E.I. DuPont de Nemours, Inc.

TABLE 3
Gurley Numbers

Sample ID	Thickness (mm)*	Base Material Gurley No. (sec)	Final Swollen Membrane Gurley Number (sec)
Example 1	0.02	2-4	Total occlusion
Example 2	0.02	2-4	Total occlusion
Example 3	0.01	2-4	Total occlusion
Example 4	0.01	2-4	Total occlusion
Example 5	0.01	2-4	Total occlusion

10 *Thickness measurements were obtained on samples prior to swelling in
dried state.

TABLE 4
Ionic Conductance

Sample ID*	Ionic Conductance (micromhos/minute)
Example 1	119 (swollen)
Example 6	5.1 (unswollen)
Nafion 115	15.9 (swollen)

TABLE 5
Strength Modulus

Sample ID	Thickness (mm)	Strength Modulus (lb per dry sq. in.)**
Example 1	0.02*	15150
Nafion 115	0.13	12750

*Thickness measurements were obtained prior to swelling in dried state.

**Strenght modulus measurements were obtained in the swollen state.

TABLE 6
Percent Linear Expansion

Sample ID	Unswollen (x) (mm)	Swollen (x) (mm)	Average % Expansion in x-direction	Unswollen (y) (mm)	Swollen (y) (mm)	Average % Expansion in y-direction
Example 1	124.4	124.4	--	123.3	123.3	--
Nafion 117	125.5	137.7	+9.7	127.3	149.7	+17

TABLE 7
Percent Weight Change

Sample ID	Unswollen wt (g)	Swollen wt (wet) (g)	% weight change (wet)
Example 1	0.2515	1.0273	+308%
Nafion 117	5.5700	7.5106	+35%

WE CLAIM:

1. A composite membrane consisting essentially of:
 - (a) a microporous polymeric sheet; and
 - 5 (b) an ion-exchange material which substantially occludes the micropores of said polymeric sheet, so that the composite membrane is impermeable to fluids.
2. The composite membrane of Claim 1 wherein the ion-exchange material is a polymer.
- 10 3. The composite membrane of Claim 1 wherein the microporous polymeric sheet is selected from polymeric sheets of polyolefins, polyamides, polycarbonates, cellulose, polyacrylates, copolyether esters, copolyether amides, chitosan, and fluoropolymers.
4. The composite membrane of Claim 3 wherein the microporous polymeric
15 sheet is polytetrafluoroethylene and the ion-exchange material is a perfluorinated polymer.
5. The composite membrane of Claim 4 wherein the perfluorinated ion-exchange resin is a cationic ion-exchange resin.
6. The composite membrane of Claim 5 wherein the perfluorinated ion-
20 exchange resin is a carboxylic ion-exchange resin.
7. The composite membrane of Claim 5 wherein the perfluorinated ion-exchange resin is a sulfonic ion-exchange resin.
8. The composite membrane of Claim 1 which contains a finely divided powder.
- 25 9. The composite membrane of Claim 1 wherein the membrane is less than 50 microns thick.
10. The composite membrane of Claim 1 wherein the composite is attached to a support backing.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/07175

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D69/12 B01D71/06 B01D61/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	<p>WO 96 28242 A (GORE & ASS) 19 September 1996 cited in the application see page 3, line 12 - page 3, line 33 see page 4, line 21 - page 9, line 23 see claims 1-9; examples 1-23; tables 1-7 --- -/-</p>	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
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- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- * "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- * "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- * "&" document member of the same patent family

Date of the actual completion of the international search

22 September 1997

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/07175

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 692 569 A (GROT WALTHER GUSTAV) 19 September 1972 see column 1, line 15 - column 1, line 24 see column 2, line 18 - column 3, line 34 see column 4, line 1 - column 4, line 75 see column 5, line 26 - column 5, line 73 see column 6, line 4 - column 6, line 7; claims 1,5,7	1-5,7,9
Y	see column 1, line 15 - column 1, line 24 see column 2, line 18 - column 3, line 34 see column 4, line 1 - column 4, line 75 see column 5, line 26 - column 5, line 73 see column 6, line 4 - column 6, line 7; claims 1,5,7	6,8,10
Y	GB 2 009 788 A (GEN ELECTRIC) 20 June 1979 cited in the application see page 3, line 34 - page 3, line 64 see page 4, line 3 - page 4, line 13	6,8,10
Y	EP 0 579 852 A (JAPAN GORE TEX INC) 26 January 1994 see page 2, line 50 - page 3, line 58; claims 1-3	8
X	US 5 082 472 A (MALLOUK ROBERT S ET AL) 21 January 1992 cited in the application see column 6, line 52 - column 6, line 59 see column 9, line 22 - column 9, line 24 see column 12, line 25 - column 12, line 28; claims 8,17,18; figure 3	1-7
A	US 5 094 895 A (BRANCA PHILLIP A ET AL) 10 March 1992 cited in the application see the whole document	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 97/07175

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9628242 A	19-09-96	US 5547551 A	20-08-96
		US 5599614 A	04-02-97
		AU 4897196 A	02-10-96
		FR 2731631 A	20-09-96
		US 5635041 A	03-06-97

US 3692569 A	19-09-72	NONE	

GB 2009788 A	20-06-79	US 4210501 A	01-07-80
		US 4224121 A	23-09-80
		AR 225606 A	15-04-82
		AU 519593 B	10-12-81
		AU 4239378 A	14-06-79
		AU 518335 B	24-09-81
		AU 4239478 A	28-06-79
		BE 872632 A	08-06-79
		BE 872634 A	08-06-79
		CA 1152451 A	23-08-83
		CA 1125697 A	15-06-82
		CH 645552 A	15-10-84
		CH 650032 A	28-06-85
		DE 2844495 A	13-06-79
		DE 2844499 A	13-06-79
		DE 2857627 C	30-12-82
		FR 2411029 A	06-07-79
		FR 2411248 A	06-07-79
		GB 2009792 A,B	20-06-79
		GB 2071157 A,B	16-09-81
		IN 150899 A	08-01-83
		JP 59064789 A	12-04-84
		JP 1285250 C	09-10-85
		JP 54093690 A	24-07-79
		JP 58054611 B	06-12-83
		JP 1370075 C	25-03-87
		JP 54095996 A	28-07-79
		JP 61027472 B	25-06-86
		NL 7811995 A	12-06-79
		NL 7811996 A	12-06-79
		SE 453518 B	08-02-88
		SE 7812639 A	02-08-79

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US 97/07175

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2009788 A		SE 7812641 A	10-06-79
		ZA 7805566 A	26-03-80
		ZA 7805586 A	26-09-79
		AU 518219 B	17-09-81
		AU 4239178 A	28-06-79
		BE 872633 A	08-06-79
		CA 1137022 A	07-12-82
		CH 650031 A	28-06-85
		DE 2844496 A	13-06-79
		FR 2411249 A	06-07-79
		GB 2009795 A,B	20-06-79
		IN 150786 A	18-12-82
		JP 1389151 C	14-07-87
		JP 54112398 A	03-09-79
		JP 61006156 B	24-02-86
		JP 58181879 A	24-10-83
		NL 7811997 A,B, --	12-06-79
		SE 453602 B	15-02-88

EP 0579852 A	26-01-94	US 5190813 A	02-03-93

US 5082472 A	21-01-92	AU 654098 B	20-10-94
		AU 8842391 A	26-05-92
		EP 0556232 A	25-08-93
		JP 2578281 B	05-02-97
		JP 6503258 T	14-04-94
		WO 9207649 A	14-05-92

US 5094895 A	10-03-92	AU 628580 B	17-09-92
		AU 5643790 A	29-11-90
		CA 2049327 A	29-10-90
		EP 0470186 A	12-02-92
		JP 7103251 B	08-11-95
		JP 4507112 T	10-12-92
		WO 9013593 A	15-11-90
		US 5183545 A	02-02-93
